



## Disinfection of urine by conductive-diamond electrochemical oxidation

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### ARTICLE INFO

#### Keywords:

Disinfection  
Electrolysis  
*E. coli*  
*P. aeruginosa*  
Diamond

### ABSTRACT

This work focuses on the application of electrolysis with diamond anodes for the disinfection of urine. To do this, a synthetic human urine was polluted with *Escherichia coli* and *Pseudomonas aeruginosa* and then, it was electrolyzed at current densities within the range 0–100 A m<sup>-2</sup>. Results show that it is possible to disinfect completely the effluent even at applied electric charges lower than 2 kAh m<sup>-3</sup>, regardless the current density applied. This good performance is related to the production of powerful oxidants from the oxidation of the ions present in synthetic urine. Likewise, these species also react with the organics contained in urine (urea, creatinine and uric acid), favoring their degradation. The process efficiency for both microorganisms and organics is higher when working at low current densities. The removal of organics leads to the release of significant amounts of nitrogen in the form of nitrate which are later electroreduced to ammonium, that, in turn, reacts with the electrogenerated hypochlorite, favoring the production of chloramines (which can also contribute to the disinfection process). Regarding the mineralization, TOC removal higher than 90% can be achieved but higher applied electric charges than those required for disinfection have to be applied (around 30 kAh m<sup>-3</sup>).

### 1. Introduction

In last decades, electrochemical disinfection has been widely studied for the treatment of drinking water and reclaimed wastewater (secondary effluents coming from Wastewater Treatment Plants, WWTPs) [1–3]. Specifically, this technology has been proven very efficient for the removal of the *Escherichia coli* (*E. coli*) contained in these effluents, because of the electrochemical production of disinfectants from the oxidation of ions naturally contained in water [4–9]. For this reason, it was not necessary the addition of chemicals to carry out an efficient treatment as occur during conventional disinfection processes and, therefore, the main physical-chemical characteristics of water and wastewater were not significantly altered [10].

One of the keys in electrochemical disinfection is the choice of a suitable electrode that favors the potential production of disinfectant species. In this context, Boron Doped Diamond (BDD) can be considered as an appropriate anode material because it allows to generate large amounts of these species in-situ, favoring the disinfection processes, even at low applied electric charges and current densities [11–15]. Likewise, these electrodes promote the generation of significant amounts of hydroxyl radicals by means of water oxidation [16]. These species have a high oxidant capacity which may contribute to the disinfection processes. Therefore, the use of BDD anodes does not only

favor efficient disinfection processes but also helps to decrease the energy consumption in the disinfection of water and reclaimed wastewater [17].

On the other hand, more recently, the scientific community has begun to focus attention on the disinfection of urine in hospitals and other facilities [18–21]. An important volume of these urines may present high pathogenicity, associated to different diseases and this is becoming a key point because of the appearance of antibiotic-resistant bacteria. In this context, the World Health Organization (WHO) has recently reported a priority list of antibiotic-resistant bacteria and, as an example, WHO considers *Pseudomonas aeruginosa* as priority 1 (critical), *Staphylococcus aureus* as priority 2 (high) or *Streptococcus pneumoniae* as priority 3 (medium). Therefore, hospital effluents should be also properly treated in order to preserve not only the human health but also the environment, because there is no currently legislation for this type of hazardous effluents.

In literature, it has been recently reported the disinfection of human urine with BDD anodes. Specifically, Raut et al. have studied the removal of *E. coli* in human urine for water-free and additive-free toilets by electrolysis [22]. They evaluated the elimination of microorganisms at different cell voltages (4–12 V), finding that it was possible to attain a complete disinfection at operation times lower than 1 h. The higher voltage led to the higher removal rate of *E. coli* due to the generation of

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large amounts of free chlorine. They also evaluated the removal of microorganisms in human urine with fecal pollution at 6 V and they demonstrated that the presence of high concentration of fecal matter was negative for disinfection efficiency. However, the evolution of the organics from urine was not studied in that work. This is an important point taking into account that the electrogenerated free chlorine can react with these organics, favoring the formation of hazardous organochlorinated compounds.

With this background, the main aim of the present work is to evaluate the disinfection of urine that can be typically found in hospital wastewater by electrolysis with diamond electrodes, paying special attention not only to the removal of microorganisms but also to the evolution of organics present in wastewater and, hence, to the mechanisms of the processes involved. To do this, synthetic urine was polluted with *E. coli* and, also, *P. aeruginosa*. The last one has been selected because it is one of the bacteria reported by WHO as critical priority, while the first one is the most common indicator of fecal pollution and it is the most frequent pathogen in urine. The influence of the current density ( $0\text{--}100 \text{ A m}^{-2}$ ) has been studied because this parameter is expected to influence on the electrochemical process efficiency.

## 2. Material and methods

### 2.1. Chemicals and microorganisms

Urea, creatinine, uric acid, potassium chloride, magnesium sulfate, calcium phosphate, sodium carbonate and diammonium hydrogen phosphate were analytical grade and used as received (Sigma Aldrich, Spain). Acetonitrile and formic acid HPLC grade (Sigma Aldrich, Spain) were used for the mobile phase to determine uric acid. p-dimethylaminobenzaldehyde and hydrochloric acid (Sigma Aldrich, Spain) were analytical grade and used for the determination of urea concentration. Acetone, 2,6-pyridinedicarboxylic acid and nitric acid (Sigma Aldrich, Spain) were used for the mobile phase to determine creatinine and ions concentration. Double deionized water (Millipore Milli-Q system, resistivity:  $18.2 \text{ M}\Omega \text{ cm}$  at  $25^\circ\text{C}$ ) was used to prepare all solutions.

The bacterial strains used in this work were *E. coli* ATCC 25922 and *P. aeruginosa* NCIMB 8626 (CECT, Spain).

### 2.2. Analytical techniques

The concentration of *E. coli* and *P. aeruginosa* was estimated by filtration with membrane according to ISO 9308-1 and ISO 16266, respectively. Sodium thiosulphate was added to the samples for the determination of microorganisms in order to avoid their death by the attack of the electrogenerated oxidants after the treatment. Measurements were done in triplicate. Samples were diluted with 0.9% NaCl aqueous solution and  $50 \text{ cm}^3$  were filtered by  $0.45 \mu\text{m}$ . Then, membranes were spread in plates with selective agar for each microorganism (Scharlau, Spain) and were incubated at  $37^\circ\text{C}$  during 24 h. Finally, colonies were counted.

Uric acid concentration was measured by chromatography using an Agilent 1200 series chromatograph equipped with a DAD detector and a ZORBAX Eclipse Plus C18 analytical column. The mobile phase consisted of 98:2 v/v aqueous solution with 0.1% of formic acid/acetonitrile (flow rate:  $1 \text{ cm}^3 \text{ min}^{-1}$ ). The DAD detection wavelength was 235 nm, the temperature was kept at  $25^\circ\text{C}$  and the injection volume was  $10 \mu\text{L}$ . Urea concentration was determined by a spectrophotometric method using the Cary Series UV-vis Spectrophotometer (Agilent Technologies). It is based on the yellow-green color produced when p-dimethylaminobenzaldehyde is added to urea in dilute hydrochloric acid solution [23]. The concentration of trihalomethanes (THMs) was measured by gas chromatography using a Young Lin GC 6100 series chromatograph equipped with an ECD detector and a SPB-5 column ( $30\text{m} \times 0.25 \text{ mm}$ ). Nitrogen was used as carrier gas and the

temperature ramp was  $50^\circ\text{C}$  for 5 min,  $6^\circ\text{C min}^{-1}$  up to  $150^\circ\text{C}$  and hold time 5 min. The injection volume was  $1 \mu\text{L}$ .

Total Organic Carbon (TOC) was monitored using a Multi N/C 3100 Analytik Jena analyzer. Inorganic ions were measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. A Metrosep A Supp 7 column was used to determine the anions and a Metrosep A Supp 4 column was used to analyze the cations. The mobile phase consisted of 85:15 v/v 3.6 mM  $\text{Na}_2\text{CO}_3$ /acetone solution for the determination of anions (flowrate:  $0.80 \text{ cm}^3 \text{ min}^{-1}$ ) and 1.7 mM  $\text{HNO}_3$  and 1.7 mM 2,6-pyridinedicarboxylic acid solution for the determination of cations (flowrate:  $0.90 \text{ cm}^3 \text{ min}^{-1}$ ). The temperature of the oven was 45 and  $30^\circ\text{C}$  for the determination of anions and cations, respectively. The volume injection was  $20 \mu\text{L}$ . The same system of cations determination was used for the quantification of creatinine concentration. Oxidants were determined iodometrically according to Kolthoff & Carr [24]. The pH and conductivity were measured using a CRISON pH25+ and CRISON CM35+, respectively.

### 2.3. Experimental procedure

Electrolyses were carried out in a single compartment electrochemical cell working under batch-operation mode [25]. Circular boron doped diamond (BDD) plates (purchased from WaterDiam, France) with a geometric area of  $78 \text{ cm}^2$  were used as electrodes, and the inter-electrode gap between both electrodes was 9 mm. A Delta Electronika ES30-10 power supply (0–30 V, 0–10 A) provided the electric current.

All experiments were carried out under galvanostatic conditions and the current densities applied were within the range  $0\text{--}100 \text{ A m}^{-2}$ . The synthetic urine was stored in a glass tank ( $1 \text{ dm}^{-3}$ ) and its composition is detailed in Table 1.

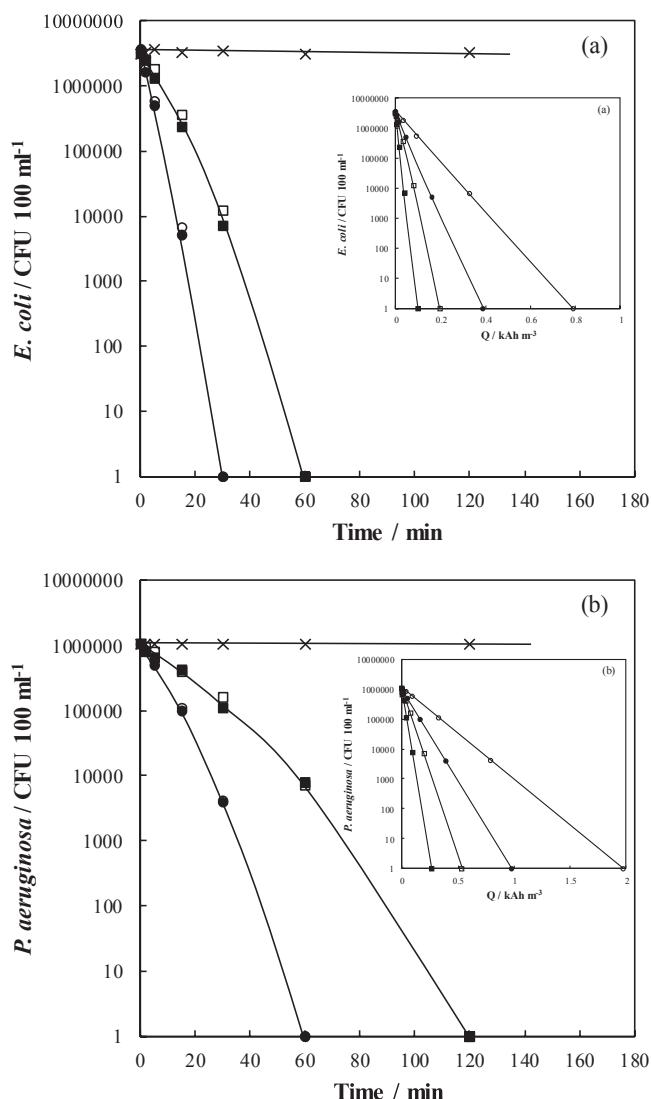
## 3. Results and discussion

Fig. 1 shows changes in concentration of *E. coli* (Fig. 1a) and *P. aeruginosa* (Fig. 1b) with the operation time and the applied electric charge (onset) during the electrochemical disinfection of synthetic urine using diamond electrodes.

As it can be observed, the concentration of both microorganisms remains constant during the reference test (process without electric power). These results reveal that the complex matrix of synthetic urine (inorganic and organic compounds) does not affect to *E. coli* and *P. aeruginosa* concentration within the experimental period evaluated. On the contrary, it is possible to attain a complete disinfection of the urine for all the tests carried out applying current densities within the range  $5\text{--}100 \text{ A m}^{-2}$ . Nonetheless, the process is clearly influenced by this parameter and the initial bacteria concentration. In this context, the removal rate of both microorganisms increases when working at current densities higher than  $50 \text{ A m}^{-2}$ . Opposite to that, if results are plotted against the electric charge (onset), it can be seen that the disinfection efficiency increases when the current density decreases. Specifically, the highest efficiency is achieved at  $5 \text{ A m}^{-2}$  for both *E. coli* and *P. aeruginosa* removal. This is an expected behavior in electrochemical

**Table 1**  
Synthetic urine composition.

Compound	Concentration ( $\text{mg dm}^{-3}$ )
$\text{CH}_4\text{N}_2\text{O}$	3333.34
$\text{C}_4\text{H}_7\text{N}_3\text{O}$	166.67
$\text{C}_5\text{H}_4\text{N}_4\text{O}_3$	50.00
KCl	1000.00
$\text{MgSO}_4$	170.00
$(\text{Ca})_3(\text{PO}_4)_2$	28.34
$\text{Na}_2\text{CO}_3$	166.67
$(\text{NH}_4)_2\text{HPO}_4$	83.34



**Fig. 1.** Variation of microorganisms as function of the operation time and the applied electric charge during the electrochemical disinfection of synthetic urine with diamond electrodes. (a) *E. coli*; (b) *P. aeruginosa*; (x) 0 A m⁻²; (■) 5 A m⁻²; (□) 10 A m⁻²; (●) 50 A m⁻²; (○) 100 A m⁻².

processes which are typically more efficient at lower current densities because of the prevention of side reactions at these softer operation conditions [26].

On the other hand, it is important to point out that the removal of *E. coli* is faster than that obtained for *P. aeruginosa*, despite the concentration of the first one is higher. Specifically, *E. coli* is depleted before 60 min for all the current densities studied whereas *P. aeruginosa* requires operation times higher than 60 min to achieve a complete removal. This fact may be directly related to the higher initial concentration of *E. coli* present in the urine. Likewise, *P. aeruginosa* could give more resistance to the electrochemical treatment due to its characteristics since it is important to highlight that this bacterium is considered as antibiotic-resistant bacteria.

For comparison purposes, the results obtained for both microorganisms were fitted to first order kinetics and the resulting constants (*k*) are presented in Table 2. These values clearly reveal the rapid removal of *E. coli* in comparison with *P. aeruginosa*.

The kinetic constants calculated for the *E. coli* are approximately two times the values obtained for the *P. aeruginosa*. Hence, the higher initial concentration of microorganisms, the higher is the removal rate. On the other hand, it can be seen that the resulting constants for low (5

**Table 2**  
Kinetic constants for the electrochemical disinfection with BDD anodes.

Microorganism	j (A m⁻²)	k (min⁻¹)
<i>E. coli</i>	5	0.1956
	10	0.1768
	50	0.4314
	100	0.4055
<i>P. aeruginosa</i>	5	0.0802
	10	0.0785
	50	0.1803
	100	0.1757

and 10 A m⁻²) and high (50 and 100 A m⁻²) current densities are similar between them for each microorganism. Furthermore, the values for 50 and 100 A m⁻² are about two times higher than that obtained during the electrochemical disinfection at 5 and 10 A m⁻², regardless the bacteria studied.

According to literature, the removal of microorganisms may take place by different mechanisms during the electrochemical treatment: direct and mediated disinfection. During the first one, an electro-adsorption of microorganisms takes place on the electrode surface, causing their death by electrocution. However, this mechanism is expected in porous materials such as carbon felt, foams, cloth [27] and, therefore, it can be discarded for the electrochemical disinfection with diamond electrodes. The second mechanism, indirect disinfection, consists of the attack of disinfectant species (usually chlorine derivatives) to microorganisms contained in wastewater. These species can be directly added to the effluent or be generated in situ during the treatment [28–30]. In this context, the composition of the synthetic urine used in this work presents large amounts of chlorides which can be electrooxidized, favoring the production of chlorine and hypochlorite [Eqs. (1)–(3)] [4,31]. Furthermore, other ions can be found in synthetic urine (sulfate, phosphate, carbonate,...) which can be also electrochemically oxidized, generating powerful oxidants such as persulfate [Eq. (4)], peroxodiphosphate [Eq. (5)] and percarbonate [Eq. (6)] [32].



These compounds can significantly contribute to the removal of the pathogens contained in urine. Fig. 2 shows the oxidants electro-generated at the end of the electrochemical disinfection of synthetic urine as function of the applied current density.

As it can be observed, the concentration of oxidants increases with the applied current density. This behavior may be directly related to the higher removal rate of microorganisms when working at higher current densities (Fig. 1). Hence, the higher the concentration of oxidants produced, the higher is the removal rate of microorganisms. On the other hand, it is important to point out that the cocktail of oxidants electrogenerated during the treatment of synthetic urine leads to a more efficient disinfection process than that observed, for example, during the disinfection of secondary effluents from Wastewater Treatment Plants (WWTP) [14]. In that case, the disinfection is mainly produced by the generation of chlorine disinfectants because of chloride is the primary ion contained in those effluents whereas the concentration of others such as phosphate, or sulfate is negligible. Therefore, the presence of other ions in urine and, consequently, in hospital effluents may significantly contribute to a more efficient disinfection. This has been also recently reported by the authors for the efficiency of the electro-

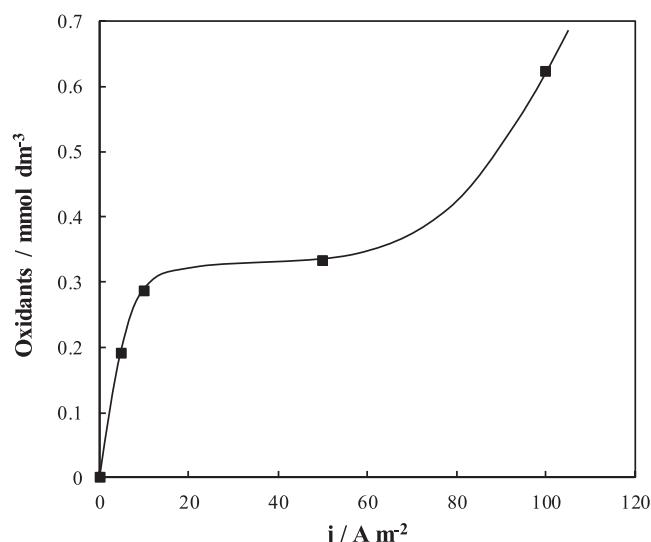
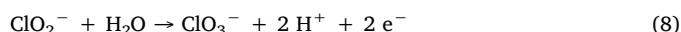
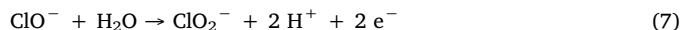


Fig. 2. Final concentration of oxidants electrogenerated as function of the current density during the electrochemical disinfection of synthetic urine with diamond electrodes.

oxidation during the treatment of soil washing effluents [33]. Finally, the results obtained shows that the final concentration of oxidants at 10 and 50 A m<sup>-2</sup> are very similar. This suggests that these species are wasted not only in disinfection but also in other oxidation processes when working at current densities higher than 50 A m<sup>-2</sup>.

The electrooxidation of chlorides contained in the synthetic urine ([Cl<sup>-</sup>]<sub>0</sub>: 475.53 mg dm<sup>-3</sup>) does not only lead to the generation of hypochlorite during electrolysis with diamond anodes but, unfortunately, it is also possible to produce electrochemically other chlorine compounds in high oxidation state such as chlorate and perchlorate [Eqs. (7)–(9)] [34,35]. These species are harmful to human health and environment, and hence, they should be avoided. For this reason, the concentration of chlorine compounds was monitored during the process and results are shown in Fig. 3.



As expected, the concentration of hypochlorite (Fig. 3a) increases with the applied electric charge during all the tests carried out, regardless the current density applied. The trend observed clearly indicates that there are two different zones: an initial increase followed by a further decrease. The first one (increase) is due to the electrolysis of chlorides present in synthetic urine [Eqs. (1)–(3)] and the decrease observed is related to different processes that can take place simultaneously during the electrochemical treatment:

- The promotion of hypochlorite to other chlorine compounds in higher oxidation state [Eqs. (7)–(9)].
- The reaction of hypochlorite with other compounds contained in the effluent, including microorganisms.

The evolution of chlorine compounds in higher oxidation state than hypochlorite is presented in Fig. 3b, specifically, the concentration of chlorate. At this point it is important to highlight that the presence of perchlorate was not detected for all the tests carried out. This fact can be explained in terms of the low current densities used in this work in comparison to those required for the electrochemical production of perchlorates with diamond anodes [36].

As it can be seen, the concentration of chlorate increases with the applied electric charge, being significantly influenced by the current density: the higher current density, the higher concentration of

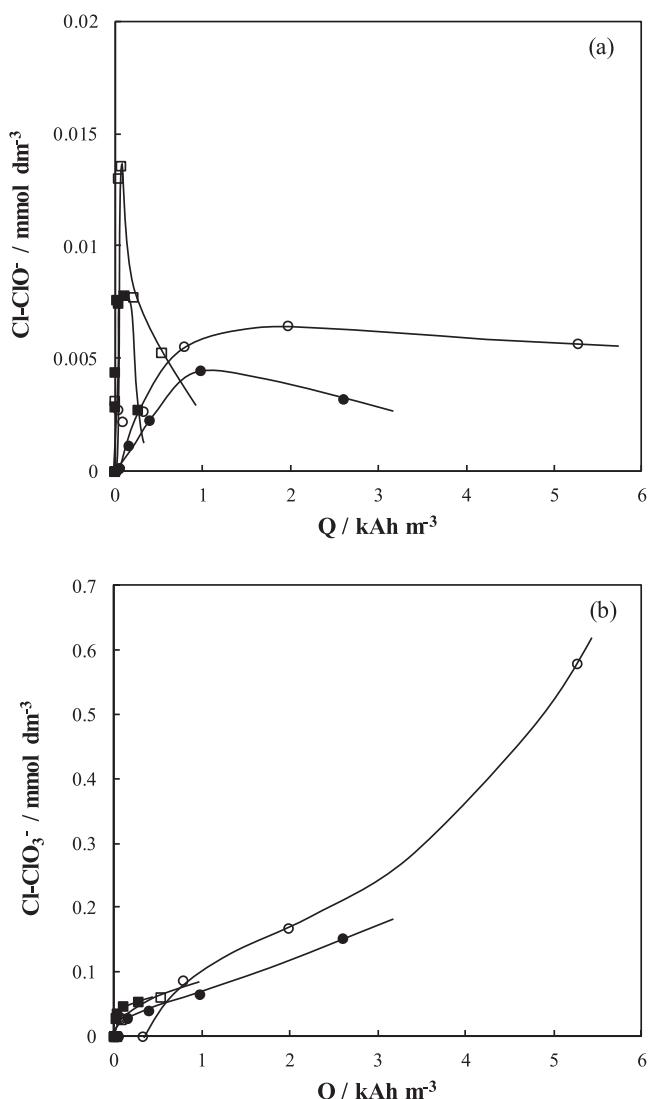
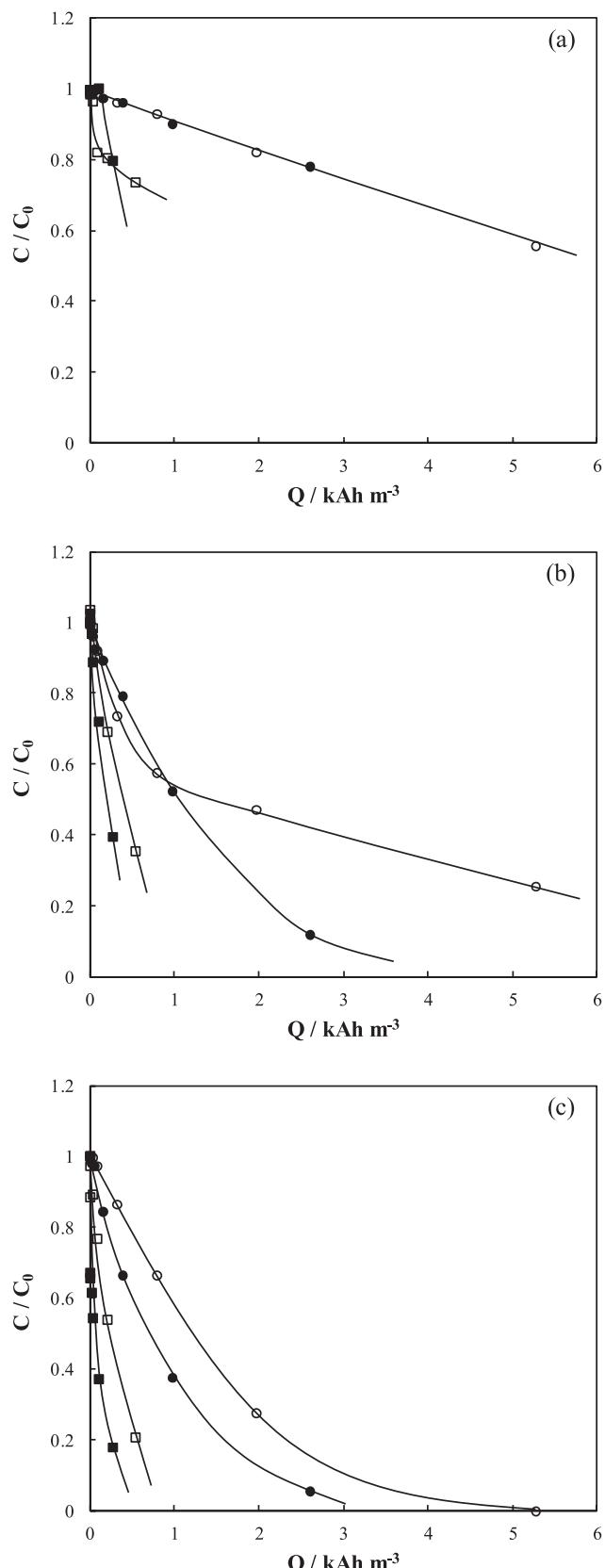


Fig. 3. Inorganic chlorine speciation during the electrochemical disinfection of synthetic urine with diamond anodes. (a) ClO<sup>-</sup>; (b) ClO<sub>3</sub><sup>-</sup>; (■) 5 A m<sup>-2</sup>; (□) 10 A m<sup>-2</sup>; (●) 50 A m<sup>-2</sup>; (○) 100 A m<sup>-2</sup>.

chlorate. This result indicates that the production of this compound takes mainly place by an electrochemical process. At low current densities, the maximum concentration of chlorate reached was 0.054 (5 A m<sup>-2</sup>) and 0.060 (10 A m<sup>-2</sup>) mmol Cl dm<sup>-3</sup> whereas 0.151 and 0.579 mmol Cl dm<sup>-3</sup> were obtained when working at 50 and 100 A m<sup>-2</sup>, respectively. These latter data (high current densities) are more negative due to their high concentrations (> 0.1 mmol Cl dm<sup>-3</sup>) and could limit the application of electrolysis with diamond anodes for the disinfection of hospital effluents. Nonetheless, the applied electric charge required to attain these values are higher than those necessary to completely disinfect the effluent and, hence, the potential production of these hazardous chlorine compounds could be avoided.

The second process that could explain the decrease observed in hypochlorite concentration is its reaction with other compounds present in the effluent. In this context, urine matrix contains different organics which are susceptible to react with hypochlorite and with other electrogenerated oxidants. For this reason, the concentration of urine-organic-compounds was monitored during the process. It is important to pay attention to the evolution of these compounds not only for their possible reaction with hypochlorite but also because, as organics, it is necessary to decrease their concentration in the effluents. Thus, Fig. 4 shows the concentration of urea, creatinine and uric acid with the



**Fig. 4.** Influence of the current density on organic compounds during the electrochemical disinfection of synthetic urine with diamond anodes. (a) urea; (b) creatinine; (c) uric acid; (■) 5  $\text{A m}^{-2}$ ; (□) 10  $\text{A m}^{-2}$ ; (●) 50  $\text{A m}^{-2}$ ; (○) 100  $\text{A m}^{-2}$ .

applied electric charge during the electrolysis of synthetic urine with diamond anodes.

As it can be observed, the concentration of organics decreases with the applied electric charge for all the current densities studied. However, as previously commented on disinfection (Fig. 1), the process efficiency is higher when working at low current densities [26]. On the other hand, the removal rate is higher in uric acid followed by creatinine and, finally, urea.

This fact may be related to the different initial concentration of each one in urine: the concentration of uric acid and creatinine is about 67 and 20 times lower than that of urea, respectively. These results disagree the previous obtained for microorganisms removal where the higher concentration of *E. coli* as compared to *P. Aeruginosa* led to the higher disinfection efficiency. Nevertheless, in this case, the differences between both microorganisms was only around 3 times (Fig. 1). Regarding the data obtained at the applied electric charges in this work (j: 5  $\text{A m}^{-2}$ ,  $Q_{\max}$ : 0.267  $\text{kAh m}^{-3}$ ; j: 10  $\text{A m}^{-2}$ ,  $Q_{\max}$ : 0.533  $\text{kAh m}^{-3}$ ; j: 50  $\text{A m}^{-2}$ ,  $Q_{\max}$ : 2.6  $\text{kAh m}^{-3}$ ; j: 100  $\text{A m}^{-2}$ ,  $Q_{\max}$ : 5.267  $\text{kAh m}^{-3}$ ), it is possible to completely remove the concentration of uric acid at 100  $\text{A m}^{-2}$  (Fig. 4c). Nonetheless, the trend observed for the other current densities suggests that a complete removal of this organic would be attained. Likewise, the same behavior can be observed in the evolution of creatinine for all the current densities studied (Fig. 4b). Finally, the urea concentration seems to require higher electric charges to attain a noteworthy decrease at these current densities (5–100  $\text{A m}^{-2}$ ) due to its higher concentration in synthetic urine. Specifically, the maximum removal rate was 20.2, 26.2, 21.8 and 44.40% for 5, 10, 50 and 100  $\text{A m}^{-2}$ , respectively (Fig. 4a).

The organics present in synthetic urine contains nitrogen atoms in their structure which can be released during the electrolysis. In the literature, it has been described that nitrogen from organics is initially oxidized to nitrite [Eq. (10)] [37,38]. Then, this species is rapidly transformed into nitrate [Eqs. (11) and (12)] and, finally, this last one can be electrochemically reduced over the cathode surface, favoring the production of ammonium [Eqs. (13) and (14)] [39]. To confirm that this applies to urine electrolysis, the evolution of nitrate and ammonium was monitored during the electrochemical disinfection. Nitrites were not detected during the whole process, probably because of its fast reaction to nitrates and, therefore, they are not shown.

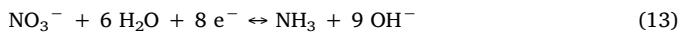
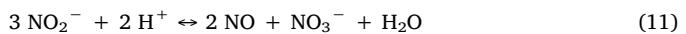


Fig. 5 shows the concentration of inorganic nitrogen compounds with the applied electric charge during the electrochemical disinfection of synthetic urine at different current densities. As it can be observed, the concentration of nitrates increases for all the current densities (Fig. 5a). However, the values obtained are not very high and, it is necessary to apply 100  $\text{A m}^{-2}$  to attain concentrations higher than 0.1 mmol N  $\text{dm}^{-3}$ . These results agree the previous obtained in the evolution of urine organic compounds (Fig. 4) where the maximum current density led to the higher removal of urea, creatinine and uric acid and, hence, the maximum release of inorganic nitrogen.

On the other hand, the low nitrate concentration can also be related to its evolution to ammonium on the cathode surface (electro-reduction). Thus, the concentration of this species is shown in Part b of Fig. 5. It is important to highlight that the initial concentration of ammonium is not zero because it is a component of the raw synthetic urine as  $(\text{NH}_4)_2\text{HPO}_4$  ( $C_0$ : 83.34 mg  $\text{dm}^{-3}$ ). Ammonium ions decrease at the beginning of the treatment until reach electric charges around 0.5  $\text{kAh m}^{-3}$  from which their concentration starts to increase,

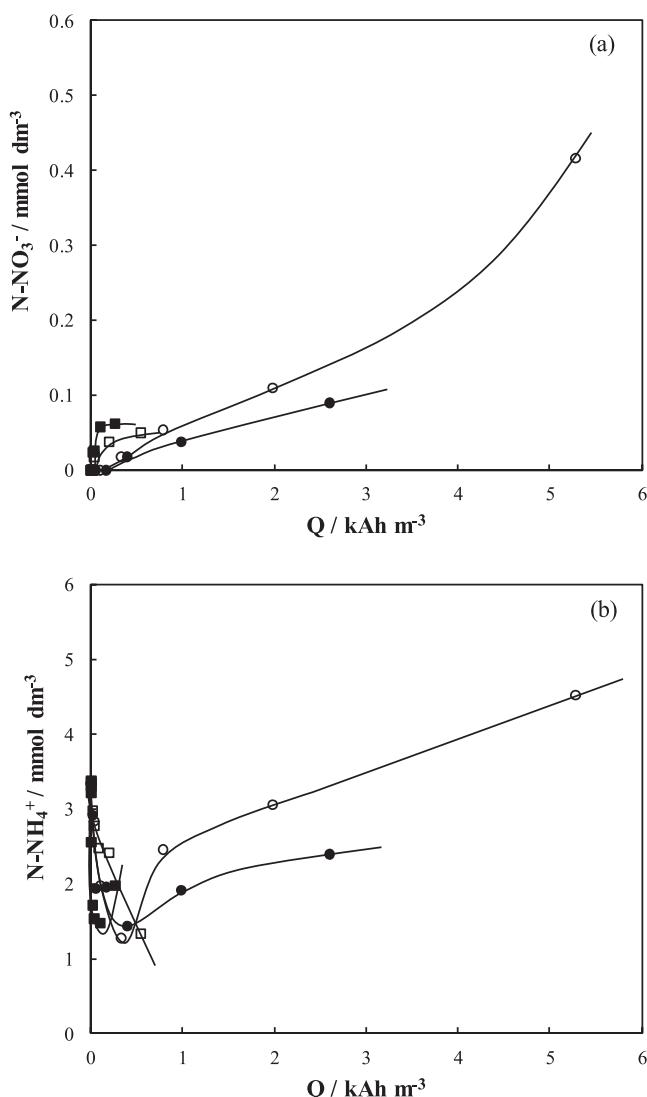


Fig. 5. Nitrogen speciation as function of applied electric charge during the electrochemical disinfection of synthetic urine with diamond anodes. (a)  $\text{NO}_3^-$ ; (b)  $\text{NH}_4^+$ ; (■) 5  $\text{A m}^{-2}$ ; (□) 10  $\text{A m}^{-2}$ ; (●) 50  $\text{A m}^{-2}$ ; (○) 100  $\text{A m}^{-2}$ .

regardless the current density applied. This behavior suggests that this species could initially react with others present in urine since the direct oxidation of ammonium with BDD electrolysis is known to be not favored [40]. In this context, the presence of chlorine compounds in high oxidation state (Fig. 3) during the process can play a key role in the evolution of ammonium, specifically, hypochlorite.

Hypochlorite is well known to react with ammonium, favoring the production of combined chlorine commonly called chloramines [Eqs. (15)–(17)]. These species also contribute to the disinfection processes but they are less aggressive than hypochlorite [12]. For this reason, the concentration of chloramines was measured for all the tests carried out, finding zero values of these species in the effluents. This means that they have reacted with microorganisms and other organics present in wastewater, favoring their degradation.



At higher electric charges, the concentration of ammonium significantly increases, reaching final values higher than the initial concentration present in synthetic urine. For example, at 100  $\text{A m}^{-2}$  the

initial and final values were 60.5  $\text{mg dm}^{-3}$  81.3  $\text{mg dm}^{-3}$ , respectively. This fact can be explained in terms of the higher release of nitrogen from the organics at these charges, which allows not only the formation of chloramines but also the production of a remaining effluent with high levels of free ammonium.

The electrolysis of urea, creatinine and uric acid can lead to the formation of other intermediates that can be even more hazardous. Some of the most harmful organic intermediate compounds which can be formed during the electrochemical disinfection in presence of free chlorine are THMs. These are generated by the reaction between hypochlorite and the organic matter contained in wastewater. The main THMs established by WHO are  $\text{CH}_3\text{Cl}$ ,  $\text{CHBrCl}_2$ ,  $\text{CHBr}_2\text{Cl}$  and  $\text{CH}_3\text{Br}$ . Therefore, the concentration of these compounds was monitored during the process and results show that only chloroform ( $\text{CH}_3\text{Cl}$ ) was generated, finding a maximum concentration of 0.036  $\mu\text{g dm}^{-3}$  of this compound at 5  $\text{A m}^{-2}$ . This value is much lower than that established by WHO for drinking water (0.3  $\text{mg dm}^{-3}$ ) [41]. Nonetheless, the final concentration reached of  $\text{CH}_3\text{Cl}$  was null for this current density. This suggests that THMs are not persistent during the disinfection of synthetic urine with diamond electrodes at low current densities. Likewise, the concentration of this compound was also null for the current densities within the range 10–100  $\text{A m}^{-2}$ .

Furthermore, it is necessary to control all the organic matter present in the system. For that, the total organic carbon (TOC) was also measured during the process. This parameter informs about the complete mineralization of the organic matter contained in the effluent. Fig. 6 shows changes in TOC concentration with the applied electric charge during the electrochemical disinfection at different current densities. As it can be observed, TOC decreases with the applied electric charge for all the tests carried out. The efficiency is higher when working at current densities lower than 10  $\text{A m}^{-2}$ . These results agree the previous obtained on the removal of microorganism (Fig. 1) and organics (Fig. 4).

The maximum TOC concentration removed was around 25% for current densities lower than 50  $\text{A m}^{-2}$  whereas 50% removal was attained when applying 100  $\text{A m}^{-2}$ . Therefore, it is not possible to achieve a complete mineralization of the organic matter contained in the effluent with the electrolysis charges applied. The trend observed in TOC is similar to the shown for urea concentration (Fig. 4a) and this is easily explained taking into account that urea is the primary organic in urine and hence it is the main species that contributes to the TOC concentration. Finally, TOC data suggest that an increase in the applied

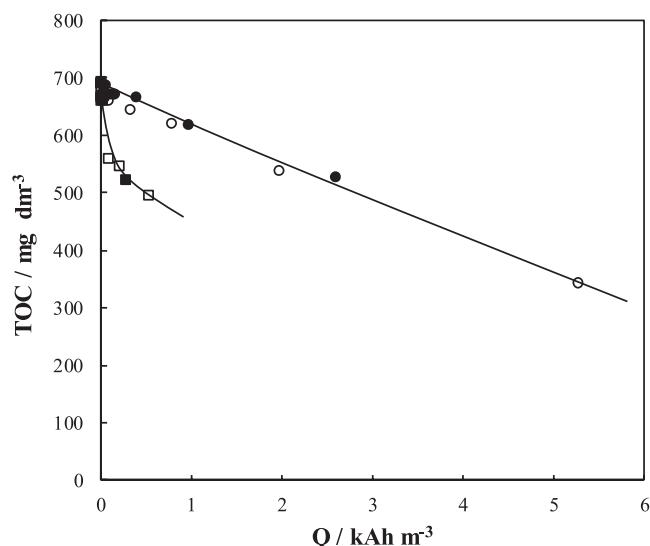
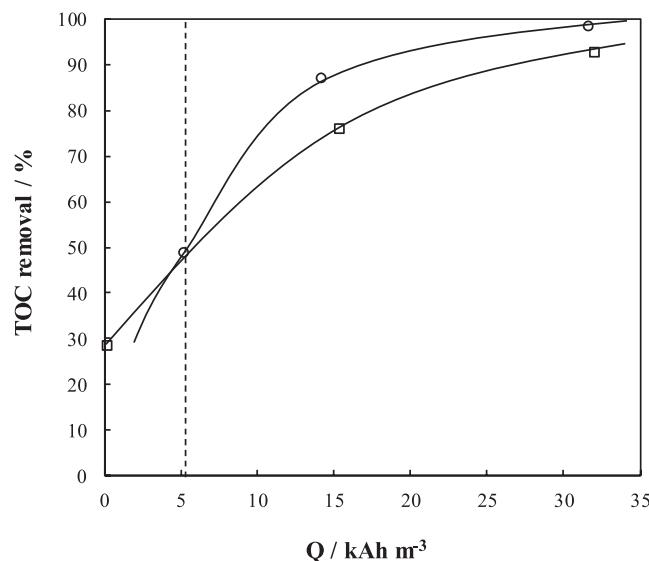


Fig. 6. TOC depletion as function of the applied electric charge during the electrochemical disinfection of synthetic urine with diamond anodes. (■) 5  $\text{A m}^{-2}$ ; (□) 10  $\text{A m}^{-2}$ ; (●) 50  $\text{A m}^{-2}$ ; (○) 100  $\text{A m}^{-2}$ .



**Fig. 7.** Final TOC concentration as function of the applied electric charge during the electrochemical disinfection of synthetic urine with diamond anodes. (□)  $10 \text{ A m}^{-2}$ ; (○)  $100 \text{ A m}^{-2}$ .

electric charge at these current densities could lead to a complete removal of the organic matter. To check this, the electrochemical disinfection of a synthetic urine was carried out at the two different current densities previously used: 10 and  $100 \text{ A m}^{-2}$ . After  $30 \text{ kAh m}^{-3}$  of electric charge passed, the removal of microorganisms (data not shown) attained was similar to than observed in Fig. 1. Regarding organics, Fig. 7 shows the maximum removal of TOC with the applied electric charge. As it can be observed, more than 90% of mineralization can be attained when the electrolysis is run during long time (electric charge passed over  $30 \text{ kAh m}^{-3}$ ). The carbon mass balance taking into account the carbon from organics (urea, creatinine and uric acid) and TOC values reveals that the formation of intermediate organic compounds are more favored when working at low current densities ( $10 \text{ A m}^{-2}$ ). This is an expected behavior because of the soft oxidation conditions at this value in comparison with the strong conditions at  $100 \text{ A m}^{-2}$  where the organics are completely mineralized. These results reveal that electrolysis with diamond anodes is a suitable technology not only for the disinfection of urine but also for the removal of the organic matter present in wastewater using low current densities.

#### 4. Conclusions

From this work, the following conclusions can be drawn:

- Electrolysis with diamond anodes allow to completely disinfect urine at applied electric charges lower than  $2 \text{ kAh m}^{-3}$  and current densities within the range  $5\text{--}100 \text{ A m}^{-2}$ . During the process, large amounts of oxidants are produced from the electrooxidation of the ions present in synthetic urine which are the main responsible of the removal of microorganisms.
- Urea, creatinine and uric acid are also degraded by the attack of electrogenerated oxidants during the electrochemical disinfection. The oxidation of these organics leads to the release of nitrogen from their chemical structure which is transformed into nitrite, nitrate and, finally, ammonium. This last one reacts with free chlorine present in the effluent, favoring the production of chloramines.
- The process efficiency is clearly influenced by the current density for both microorganisms and organics removal. In this context, low current densities ( $5\text{--}10 \text{ A m}^{-2}$ ) lead to a more efficient disinfection and degradation of urea, creatinine and uric acid from wastewater. Nonetheless, it is necessary to applied higher electric charges to

attain a complete removal of organics for all the current densities studied.

- A mineralization of the organic matter higher than 90% is achieved after passing electric charges around  $30 \text{ kAh m}^{-3}$  ( $j: 10\text{--}100 \text{ A m}^{-2}$ ). Under these conditions, it is possible to completely remove not only the concentration of microorganisms but also the urea, creatinine and uric acid concentrations by electrolysis with diamond anodes.

#### Acknowledgements

Financial support from the Spanish Ministry of Economy, Industry and Competitiveness and European Union through project CTM2016-76197-R (AEI/FEDER, UE) is gratefully acknowledged. JCCM (Junta de Comunidades de Castilla-La Mancha) is also acknowledged for the postdoctoral grant (SBPLY/16/180501/000404) awarded to Dr. Salvador Cotillas.

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